



Review

Solar disinfection is an augmentable, in situ-generated photo-Fenton reaction—Part 2: A review of the applications for drinking water and wastewater disinfection



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ABSTRACT

This is the second part of a comprehensive review article about photo-Fenton reaction at near-neutral pH used for water and wastewater disinfection. In this part, a critical revision of the fundamental physical, chemical and biological parameters affecting the photo-catalytic process efficiency are discussed. The effects of the chemical aspects, considered either as facilitators or competitors of photo-Fenton are deeply analyzed, with special focus on organic matter and its effect over bacterial inactivation. The role of solubilized iron and the biological nature of different pathogens are deeply assessed according to reported experimental data. Water temperature, turbidity, and radiation parameters like solar UV energy, light scattering and absorption during photo-Fenton are pictured in terms of treatment efficiency and suitable reactor design. Recent unconventional photo-Fenton strategies using iron chelates, iron oxides (including zero valent iron) and iron-based materials are also highlighted as new approaches to this process. Finally, the existing pilot scale studies in real conditions using photo-Fenton at near-neutral pH are revised, while alternative options and further research for real implementation are proposed.

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Abbreviations: AOP, advanced oxidation process; ARB, antibiotic-resistant bacteria; ARG, antibiotic-resistant genes; CPC, compound parabolic collector; DBPs, disinfection by-products; DOM, dissolved organic matter; EDDS, (S,S)-Ethylenediamine-N,N'-disuccinic acid; EDT, effective disinfection time; EfOM, effluent organic matter; HO•, hydroxyl radical; MWWTP, municipal wastewater treatment plant; NOM, natural organic matter; NTU, nephelometric turbidity unit; NP, nanoparticles; PET, polyethylene tetraphthalate; Q_{UV}, cumulated solar UV-A energy; ROS, reactive oxygen species; SOD, superoxide dismutase; SODIS, solar disinfection; TOC, total organic carbon; UV, ultraviolet (light); UVA, ultraviolet A (light); Vis, visible (light); ZVI, zero valent iron; NZVI, nanoscale zero valent iron; ZVINP, zero valent iron nanoparticles.

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1. Introduction

In the last decades, solar driven photocatalysis for water treatment has been investigated as an environmental friendly process to decontaminate water. In this line, photo-Fenton process raised as a promising technology for persistent organic pollutant removal. Soon after, its application for water disinfection emerged. Two main approaches can be considered when applying photo-Fenton to bacterial inactivation: drinking water disinfection and secondary effluent from municipal wastewater treatment plants (MWWTPs), for water reclamation. As for the target microorganisms, *Escherichia coli*, especially the collection strain *E. coli* K12, was the most studied bacteria. Only a few works dealt with natural enteric bacteria inactivation. Regarding the experimental scale and photo-reactor used, most of the studies were carried out at lab scale using artificial light sources or natural sun light. At pilot plant scale, tubular systems provided with compound parabolic collectors (CPC) were the most popular reactors.

The first systematic studies on photocatalytic water disinfection were based on TiO_2 for *E. coli* inactivation as an indicator microorganism [1–4]. As for photo-Fenton reactions applied to disinfection, the photoferrioxalate system was used to allow $Fe(III)$ to be dissolved at slightly acidic and near-neutral pH, concluding that photoferrioxalate was slower in inactivating microorganisms than conventional disinfectants [5]. Other attempt to use iron for water disinfection was done by Rincón and Pulgarín, who reported the enhancement in *E. coli* inactivation in fresh water by the action of $Fe(III)$ during heterogeneous photocatalysis with TiO_2 [6–8]. Later, the role of organic matter in water disinfection by photo-Fenton was also widely investigated, demonstrating the significant competition between both processes for the hydroxyl radical attack [9]. Nonetheless, this competition was not observed when highly oxidative conditions were applied during the photo-Fenton process because of the excess of radicals generated [11]. Along those early years, neutral photo-Fenton demonstrated to be more efficient than TiO_2 for water disinfection [12], not only due to the presence of low dissolved iron concentrations, but to the role that iron oxides can play in presence of H_2O_2 as an efficient heterogeneous photocatalyst for bacterial inactivation [13,14].

As for the impact of irradiance on photo-Fenton disinfection performance, different conclusions were drawn depending on the nature of the treated water and on the iron concentration employed, as both determine the light absorption properties of solution. Examples in the literature can be found in very opposite conditions, the case of well water with naturally occurring iron (0.3 mg L^{-1}) not necessarily required high solar energy doses

to achieve bacterial disinfection with *Salmonella* [15], while urban wastewater disinfection treatment (photo-Fenton at neutral pH and 20 mg L^{-1} iron) showed a first order kinetics for *E. faecalis* inactivation versus the accumulated energy [16].

The generally accepted role of *E. coli* as a surrogate of faecal contamination was examined by Spuhler et al., and they concluded that it was not an appropriate model for studying bacterial inactivation [10]. In this line, some authors started to use other species, mainly *E. faecalis*, to work on the disinfection of synthetic simulated secondary effluent of a MWWTP [17–20] as well as wild enteric bacteria of natural well water [15,21,22].

The first attempt to treat a real MWWTP secondary effluent by solar photo-Fenton at neutral pH was carried out by Klamerth et al., using the complex agent (*S,S*)-Ethylenediamine-*N,N'*-disuccinic acid (EDDS) to keep photoactive iron in solution under mild process conditions [23]. A different strategy for photo-Fenton disinfection of a real MWWTP secondary effluent in short exposure times and at natural pH was to increase the dose of iron [24].

Photo-Fenton combined with other processes was also proposed as an alternative technology for bacterial inactivation. Rodríguez-Chueca et al., reported a synergistic effect between a coagulation–flocculation–decantation (CFD) process and the photo-Fenton process at pH 5 in the inactivation of three different kinds of bacteria, usually present in MWWTP secondary effluents, [19]. The combination of solar membrane distillation and photo-Fenton to treat biologically contaminated water with *E. coli*, *Fusarium solani* and *Clostridium* sp spores, was reported by Ruiz-Aguirre et al. [25]. Giannakis et al., attempted for the first time to couple sonication and photo-Fenton for bacterial inactivation of secondary treated effluent. Ultrasound provided an additive effect in the photo-Fenton action mode, which enhanced the performance of the combined process, compared with either one of the wastewater treatments methods [26].

In this review, a practical approach of the inactivation of bacteria in secondary wastewater effluents by (solar) photo-Fenton is discussed, moving from the internal and external mechanisms affecting the bacteria inactivation already discussed in Part I of this review towards the external factors that take place in complex aqueous media. More specifically, we begin with the influence of chemical compounds which act as antagonism and synergy in the efficiency of the photo-Fenton reaction (Section 2) as well as the nature of the microorganisms. Section 3 deals with the effect of physical parameter affecting the solar reactor engineering for scaling-up from milliliters to dozens of liters. Moreover, the main unconventional photo-Fenton treatments are also presented in Section 4 to give a general view of the possible alternatives to the

Table 1

Representative chemical composition of natural waters and secondary effluents (Data from [29], [30], [20]).

	River and Lake	Secondary effluent
Cl ⁻ (mg L ⁻¹)	mg L ⁻¹ to hundreds of g kg ⁻¹ (brines)	290
NO ₃ ⁻ (mg L ⁻¹)	Tens to unities of mg L ⁻¹	12
SO ₄ ²⁻ (mg L ⁻¹)	Tens of mg L ⁻¹	115
NH ₄ ⁺ (mg L ⁻¹)	–	35
PO ₄ ³⁻ (mg L ⁻¹)	Hundreds and tens of mg L ⁻¹	6
Na ⁺ (mg L ⁻¹)	480	183
Mg ²⁺ (mg L ⁻¹)	1–100	27
K ⁺ (mg L ⁻¹)	100	24
Ca ²⁺ (mg L ⁻¹)	115	78
HCO ₃ ⁻ (mg L ⁻¹)	<250–660	86
pH	5–9	7–7.5
Conductivity (μS cm ⁻¹)	2–100	1530
Turbidity (NTU)	<50	7.78–10
TOC (mg L ⁻¹)	<10 mg C dm ⁻³	16
NOM (mg L ⁻¹)	0.1–20	
TDS (mg L ⁻¹)	<1000	250–850

traditional photo-Fenton to be applied in complex water matrices like secondary effluents. The final chapter (Section 5) presents case studies of photo-Fenton at pilot plant scale and the future research in this matter. Critical points and details on the effects that simultaneously occur during secondary effluents disinfection by solar photo-Fenton are provided.

2. Chapter I: secondary MWWTP effluents: antagonism and synergy in the photo-Fenton reaction

2.1. Differences between natural waters and secondary effluents—extrapolation from nature to man-made effluents

During the last decades, natural fresh waters are found highly polluted by human activities through the centralized MWWTP in developed countries. Conventional wastewater treatment methods consist on a combination of physical, chemical, and biological processes and operations to remove solids, organic matter and, sometimes, nutrients from wastewater prior to discharge to the environment. Therefore, MWWTP secondary effluents basically contain chemical and microbiological pollutants present by human's activities. Table 1 shows the main physico-chemical characteristic parameters of natural fresh water (mainly, rivers and lakes) and the average characteristics of the effluents from the secondary treatment of a MWWTP. Secondary effluents' compositions are highly variable in terms of load of contamination, depending on the influent quality (load and nature of its contamination) and also on the functioning of the biological (e.g. activated sludge) treatment system [27]. Secondary effluents may also contain a variety of inorganic substances from domestic and industrial sources, including a number of potentially toxic elements such as arsenic, cadmium, chromium, copper, lead, mercury, zinc, etc. Even if toxic materials are not present in concentrations likely to affect humans, they might well be at phytotoxic levels [28].

Regarding microorganisms, it should be also highlighted that beside the most known waterborne pathogens associated to secondary effluents and contaminated natural waters i.e., coliforms (total/faecal, *E. coli*), *Cryptosporidium* sp, *Giardia* cyst, *Legionella* sp, etc., other microorganisms are currently being considered “emerging pathogens”, like antibiotic-resistant bacteria (ARB). They are so-called emerging because they have recently appeared or detected in wastewater secondary effluents as a result of biological treatments of anthropogenic contaminated water and advanced detection techniques [31]. Recent studies have revealed the presence these microorganisms that represent new issues and concerns

for reuse of treated wastewater [32]. Table 2 summarized the most relevant waterborne pathogens typically detected in secondary effluents and their related human diseases and occurrence in aquatic environments (data from [33]).

Therefore, due to the presence of hazardous chemical pollutants as well as waterborne pathogens, secondary effluents should be treated prior to discharge to the environment or re-use for other activities. Recently, Ortiz-Urbe et al., highlighted the potential prospects of three technological options that will play a significant role in the sustainability of wastewater treatment, including (i) the use of membranes for both treatment of wastewater and providing high quality water from different sources and uses, (ii) the shift of biological processes to allow the self-sufficient running of MWWTPs or the recovery of value-added products and (iii) the increasing use of advanced oxidation processes (AOPs), to provide efficient means for the oxidation of recalcitrant and harmful constituents, that may be present at even very low concentrations (micropollutants) [62]. Among AOPs, the photo-Fenton process has been demonstrated to be a good option for treatment of MWWTPs secondary effluents and possibly for drinking water disinfection [63]. In a general point of view, most of the photo-Fenton reactions described in the Part I of this review for natural waters can be extrapolated for secondary effluents, since the removal of organic compounds (pollutants) and microorganisms, as well as the presence of NOM, are expected to be susceptible to degradation by photo-Fenton by the oxidative attack of hydroxyl radicals (HO•), showing a similar behavior than in natural waters [64].

NOM is the organic chemical compounds present in surface or ground water, including both humic and non-humic fractions. Humic substances (HSs) composition include aromatic and aliphatic structures, as well as carboxylic, phenolic-OH, amino and quinone groups; however, the HS composition differs from different sources as they result from microbiological, chemical and photochemical transformations of inherent plant and animal residues [65]. For drinking water, the presence of NOM is a problem due to color and taste related to these compounds; it may act as a carbon source for bacterial regrowth in potable water distribution systems, and it reduces the efficiency of water treatment operations in general. In a similar way, the high presence of organic compounds in the secondary effluents (EfOM) is a combination of autochthonous (bacterial metabolism related) and allochthonous organic matter (humic/fulvic acids of drinking water) [64,66,67]. Furthermore, EfOM may not be fully removed using conventional water treatment practices and it can react with the most commonly used disinfectant agents, such as chlorine, and other conventional wastewater treatment, like ozone, to form harmful disinfection by-products (DBPs). More specifically, trihalomethanes (THMs) and Halo Acetic Acids (HAAs) are some of the potential carcinogenic compounds generated [68]. One of the main advantages of photo-Fenton for secondary effluents treatment is its high capacity to oxidize organic matter. In addition, several works revealed the capability of this process to remove NOM from water [69,70]. It has been reported that thanks to the capability of photo-Fenton to degrade NOM, it is possible to reduce the THM formation in treated water [71–74]. This is because photo-Fenton may remove hydrophobic components predominating in the NOM from raw water [75] and low molecular weight organics between 0.5 and 4 kDa [71], which are difficult to degrade by conventional treatments.

2.2. Facilitators of the photo-Fenton reaction

The benefits of the presence of NOM for water treatment using AOPs, such as photo-Fenton have been reported [71–74]. It has been described that the main responsible for the generation of HO• by NOM in water bodies are low-molecular weight fractions, as well

Table 2
Relevant pathogens typically detected in aqueous ecosystems. Adapted from [33].

Pathogen (Human disease)	Reported in
Adenovirus (Respiratory, gastrointestinal and febrile illness)	Recreational and bathing water [34]
<i>Clostridium difficile</i> (diarrhea, colitis, toxic megacolon, ileus, sepsis)	Wastewater [35], rivers [36]
Enterovirus (Mild respiratory illness, poliomyelitis, febrile illness, meningitis, pericarditis and myocarditis, hand, foot and mouth disease)	Irrigated vegetables with contaminated water [37] MWWTP effluents [38]
<i>Escherichia coli</i> (0157) (Gastrointestinal illness, hemorrhagic diarrhoea and kidney failure)	Seawaters [39] Drinking water [40]
<i>Helicobacter pylori</i> (Acute gastritis, gastric cancer or carcinoma and peptic ulcers)	Recreational water [41] Wastewater [42]
Hepatitis A Virus (Hepatitis A)	Cattle [43], sheep, turkey and domestic animals and soil [44]
Hepatitis E virus (Hepatitis E)	Seawaters [45] Water biofilms [46]
<i>Klebsiella</i> (Pneumonia, urinary tract infections, septicemia)	Sea waters [47] MWWTP effluent [48]
<i>Legionella Pneumophila</i> (Legionnaires' disease, respiratory infections)	MWWTP effluent [49,50]
<i>Salmonella enterica</i> (Mild self-limiting gastrointestinal illness, salmonellosis, typhoid fever)	Faecal contaminated drinking water [51]
<i>Shigella sonnei</i> (Shigellosis, acute gastroenteritis, pneumonia and bloody diarrhea)	Rivers [52] Water distribution subsystems [53]
Antibiotic Resistant bacteria (ARB)	Contaminated irrigation water [54] River and seawater [55] MWWTP effluent [56]
	Fountains, lakes, swimming pools and ground water sources [57,58]
	MWWTP effluent [59,60] Seawater [61]

as the humic fraction, because of their chromophoric abilities [76,77] which favor the microbial inactivation by photo-Fenton treatment at near neutral pH [78]. Studies using model NOM, such as resorcinol, have been demonstrated that in the presence of this molecule, bacterial inactivation rate increases by photo-Fenton at near neutral pH due to an enhancement of the iron solubility in water, attributed to the presence of this organic compound. Resorcinol and its degradation intermediates form complexes with iron which are photoactive at neutral pH and therefore favor the generation of ROS for the inactivation of bacteria [10]. The beneficial role of NOM for water disinfection by photo-Fenton at near neutral pH is described widely in Part 1 of this review (Section 5). Briefly, it is suggested that the excited NOM (triplet state) can react with dissolved compounds via energy/electron or hydrogen transfer [77], and return to ground state or react with oxygen and follow a pathway similar to the one of natural organic matter [64]. Compared to natural waters, wastewaters with same dissolved organic matter levels have been suggested to produce hydroxyl radicals more efficiently [64].

Recently, it has been reported that the presence of resorcinol in water could act also as competitor for HO• generated during this AOP reducing therefore the efficiency of the process. Ortega-Gómez et al., found reduced *E. faecalis* inactivation efficiency by photo-Fenton at near neutral pH with increasing resorcinol concentrations. This effect could be due to a competition between resorcinol and bacteria for the HO• generated during both Fenton and photo-Fenton processes. Whilst under high oxidative operational conditions, i.e. excess of hydroxyl radicals generated, the competence between disinfection and photo-oxidation process was not observed [11].

2.3. Solubilization of iron in MWWTP secondary effluents

The solubility of iron in water at ferrous-ferriic chemical equilibrium is related to the pH and the redox potential. The chemical behavior of iron in water and their species formed was described in detail in Part 1 of this review. In secondary effluents the solubilization and speciation of iron will be also affected primarily by the water pH. In fact, research contributions on solar photo-Fenton for disinfection of real effluents from a secondary MWWTP have demonstrated the dramatic losses of efficiency of this process at near-neutral pH, as compared to inactivation efficiencies at acidic pH, close to optimal conditions of photo-Fenton. Case stud-

ies that show the reduced inactivation efficiency at neutral pH have been reported in real and synthetic secondary effluents for bacteria like *E. coli* and *E. faecalis* [20] as well as for more resistant water pathogens like spores of *F. solani*. This kind of microorganism is perfectly viable in acidic conditions (pH 3), as opposite to majority of coliforms bacteria that do not survive at such acidic pH values with the exception of *E. faecalis* [17]. This condition permits proper comparison of the efficiency of photo-Fenton at pH 3 and at neutral pH without any interference of pH in the survival of these spores [79]. Recent studies showed that photo-Fenton at pH around 3 lead to a <3-log concentration reduction in *F. solani* spore in secondary effluents in 2.5 h, while the concentration of these spores remained almost constant for 5 h of photo-Fenton at near-neutral pH [80] under analogous irradiance and temperature conditions.

On the other hand, as it was described in Part 1 of this review, it is accepted that at near neutral pH there is several pathways and mechanisms for which the precipitated ferric hydroxides or iron oxides formed can be relatively active for generation of hydroxyl radicals during photo-Fenton treatment, although in less proportion than the active species formed at pH 2.8. However, the low benefits observed in the inactivation efficiency of photo-Fenton treatment for secondary effluents by precipitated oxyhydroxides of iron on the generation of radicals could be masked. Rodriguez-Chueca et al. evaluated the role of precipitated iron and dissolved iron on the photo-Fenton efficiency for *E. coli* and *E. faecalis* inactivation. They tested the operational conditions of adding 10 mg L⁻¹ of Fe²⁺, and 20 mg L⁻¹ of H₂O₂, with a pH 5 in synthetic secondary effluent. Dissolved iron concentration measured was 0.05 mg L⁻¹; while the rest of the iron may have precipitated as hydrous oxyhydroxides, imparting an orange brown shade to the water. They filtered samples to remove the precipitated iron (avoiding simultaneously the color in the water) and keep only the dissolved iron in water. They found no significant differences in the inactivation of *E. coli*, but for the inactivation of *E. faecalis*, the filtered samples were inactivated faster than the unfiltered ones. These results evidenced that only dissolved iron was responsible for the inactivation of both bacteria, while precipitated iron retarded the process; which it was attributed to iron precipitated preventing light entering in the reactor [20].

On the other hand, the solubilization of iron may also be affected by the inorganic as well as organic chemical compounds, which iron can form complexes when in solution. It is known that iron

may form Fe^{3+} organo-complexes with NOM playing an important role in photo-Fenton treatment at near neutral pH [10] (see Section 5, Part 1). On the other hand, inorganic compounds such as phosphates, in photo-Fenton, sequester iron forming the corresponding non-soluble salt, which precipitates and therefore retards the reaction rate. Therefore, more iron is necessary to be added when water containing phosphates is treated by photo-Fenton. It is expected that secondary effluents will not contain phosphates; however few mg L^{-1} of this compound can be observed after the secondary treatment (see Table 1).

2.4. Competitors and inhibitors of the disinfection process

The complexity of real MWWTPs secondary effluents reduces the efficiency of photo-Fenton for water disinfection due to the presence of a number of inherent components which act as competitors against the microbial target for HO^\bullet . The competitors could be: (i) inorganic chemical compounds, (ii) organic compounds, and (iii) other microorganisms; due to the non-selectivity of the hydroxyl radicals, so this reactive oxygen species (ROS) can react with any organic compound present in the water [63].

Several authors have described the strong negative effect of the presence of carbonate (CO_3^{2-})/bicarbonate (HCO_3^-) over the Fenton reaction because these anions may react with HO^\bullet , resulting in HO^\bullet scavenging, that inhibits the oxidative attack of hydroxyl radical [3,81]. Phosphate has a double detrimental effect; first, it precipitates iron very efficiently and second, it scavenges hydroxyl radicals. Other anions present in the water, such as sulfates, nitrates and chlorides may react with iron, or with H_2O_2 or other ROS, limiting the amount of HO^\bullet generated by photo-Fenton reaction and reducing its capability to oxidize bacteria and organic matter [82,83].

Secondary effluents also contain a broad range of chemical pollutants such as pesticides, personal care products, sunscreen, pharmaceuticals, including antibiotics, etc. These organic substances may react in many ways with the generated HO^\bullet . In all cases the oxidative attack is electrophilic and the rate constants are close to the diffusion-controlled limit. The main reactions between HO^\bullet and these organic pollutants are based on: (i) hydrogen abstraction from aliphatic carbon atoms; (ii) electrophilic addition to double bonds or aromatic rings; and or (iii) electron transfer reactions [63,84]. Furthermore, other source of competition for HO^\bullet is the presence of a wide range of microorganisms naturally present in this water, which may be found at higher concentrations than the pathogenic bacteria object of study.

2.5. Influence of the nature (natural & collection) and microorganism species

Traditionally, the investigation of the capability of photo-Fenton to disinfect contaminated water has been performed using microorganisms proceeding from selected culture collections such as American Type Culture Collection (ATCC), among others. The most used collection microorganism for this research is *E. coli* K-12 due to several facts: (i) it is the most widely accepted microorganism as indicator of faecal contamination in water, (ii) it is a non-pathogenic strain; and (iii) it is relatively easy to obtain and quantify in laboratory. Moreover, *E. coli* is the water bacterium most studied for research purposes, which makes it very valuable model, as a lot of fundamental knowledge is already known about it and permits to design very focused studies on specific aspects already not explored. The use of culture collection microorganisms is useful for finding fundamental mechanistic trends between the microorganism and the reagents or compounds used in the process [10,12].

It has been described that laboratory microorganisms cultured for long periods may generate marked differences from those that exist in natural ecosystems, which also may include differences on resistance against several disinfection treatments [85]. Relocation of natural microorganisms to the laboratory can result in their adaptation to the optimized conditions for growing. This adaptation may be accompanied by complex changes in microbes, such as the repression of protective mechanisms that are essential in nature or by the long-term accumulation of mutations that lead to the gradual selection of laboratory strains. For example, microorganisms such as *E. coli*, *Salmonella* spp and *Neisseria* spp under heterogeneous environmental conditions may show diversification into specific subpopulations in terms of geno- and phenotypes. This diversification is mainly related to changes on the cells surface (membrane antigens, flagella and fimbriae), which may result in modified colonies based on altered genome rearrangements events, usually in a random manner, but may be modulated by environmental conditions [85]. Ward et al., reported the resistance of *Flavobacterium* spp in natural conditions to chlorination to be 200 times more resistant than under laboratory conditions [86]. Differences between *E. coli* K-12 and naturally occurring *E. coli* strains in wastewater effluents, in terms of their response to solar radiation stress, have been also reported using the SODIS process. Naturally occurring faecal coliforms have shown a much higher resistance to sunlight inactivation [87,88] than *E. coli* K-12 [89].

Obviously, *E. coli* K-12 strain doesn't represent the wide spectrum of naturally occurring microorganisms in secondary effluents. Among pathogenic species for human, animals and plants, the number of microorganisms vary from bacteria, coliforms and faecal coliforms such as *E. coli* and *E. faecalis* (associated with risk of human), viruses (enteroviruses, rotavirus, hepatitis A), fungi like *Fusarium* spp. and *Phytophthora* spp. (associated with pests in agriculture), to protozoa such as *Giardia lamblia* and *Cryptosporidium parvum* and parasites (*Taenia* spp. and *Ancylostoma* spp.), among others. In general, the order of resistance to disinfection treatments of different types of microorganisms is as follows: non-forming spore bacteria < fungi < viruses < forming spore bacteria < helminths < protozoa [90].

Very little research has been done on photo-Fenton at neutral pH for secondary effluents disinfection. Most of the photo-Fenton contributions describe the efficacy of this process against a specific microbiological target, such as *E. coli* [20,23,24,91], *E. faecalis* [16,20], viruses (coliphage MS2 and Echovirus) [92], *Fusarium solani* [80], while other studies have been performed following more than two naturally occurring waterborne microorganisms [20,93]. In these works, similar microbial order of resistance to solar photo-Fenton has been shown, i.e., bacteria < viruses < spores (fungi or bacteria) (Fig. 1). Agulló-Barceló et al., evaluated the inactivation of four types of naturally occurring microorganisms in real secondary effluents by photo-Fenton at pH 3 and pH 8, and solar heterogeneous photocatalysis with suspended TiO_2 , the effect of added H_2O_2 under sunlight and mere action of solar radiation in solar CPC reactors. Summarising, the naturally occurring *E. coli*, spores of sulphite-reducing clostridia (SRC), somatic coliphages (SOMCPH), and F-specific RNA bacteriophages (FRNA) showed clear differences among them in terms of inactivation kinetics. In general, order of resistance to photo-Fenton at neutral pH was: *E. coli* < FRNA < SOMCPH < SRC [93]. These results confirmed previous studies suggesting that the use of *E. coli* as a single microbial indicator might not be enough to guarantee a low risk of infection of treated secondary effluents. Ruiz-Aguirre et al., also investigated the efficacy of secondary effluent disinfection by a combination of solar membrane distillation (MD) with solar photo-Fenton. They demonstrated that this combination could be a very good alternative of secondary effluents treatment especially for highly resistant microorganisms such as SRC due to: (i) the production of a distillate

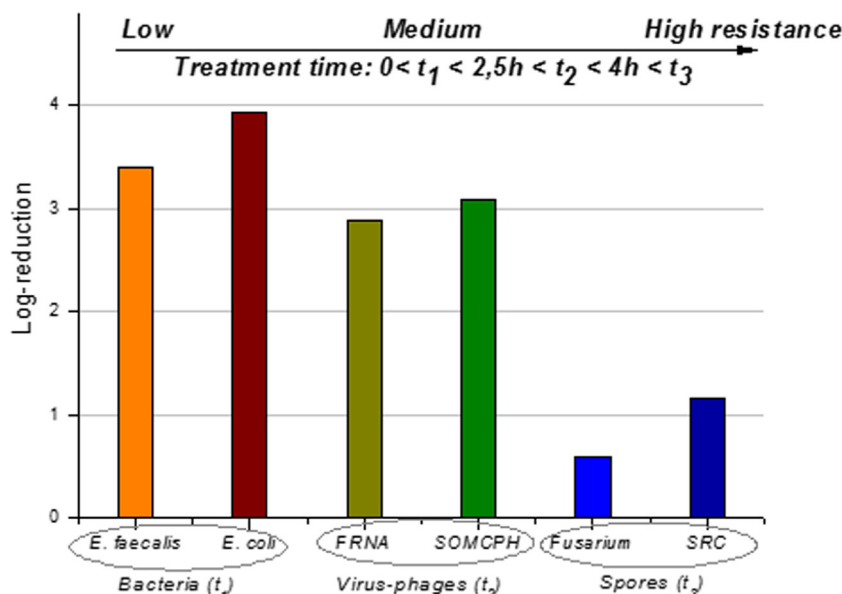


Fig. 1. Degree of resistance of several representative microbial groups (*E. faecalis*, *E. coli*, F-specific RNA bacteriophages (FRNA)), somatic coliphages (SOMCPH), *Fusarium* sp., sulphite reducing clostridia (SRC), using solar photo-Fenton (natural pH, 10–20 mg L⁻¹ of Fe²⁺ and H₂O₂) in real wastewater effluents in solar CPC reactors. (Adapted from [18,80,93]).

completely free of pathogens (it was specifically tested with *E. coli*, *F. solani* and spores of sulphite-reducing *Clostridium*, SRC), and (ii) the capability of complete removal of SRC by the combination of mechanical and thermal stress suffered inside the MD module and the oxidative attack of HO• generated by photo-Fenton [25].

This difference could be primarily attributed to their different cellular architectures. Three main points should be considered in this sense, thickness, composition and structure of external cell walls; different internal defense mechanisms available and the different basal activity among these kinds of microorganisms (vegetative cells or resistance structures).

The main difference between Gram-positive (*E. faecalis*) and Gram-negative (*E. coli*) bacteria is their cell wall. Gram-negative bacteria have a cytoplasmic membrane, a thin peptidoglycan layer and an outer membrane containing lipopolysaccharide, while Gram-positive bacteria have only a cytoplasmic lipid membrane with a thicker peptidoglycan layer, which confers more resistance to oxidative stress. Even, several reports have demonstrated a higher resistance of Gram-positive bacteria, as compared to Gram-negative, to advanced oxidation processes, as they need a larger number of oxidative attacks by OH• to complete bacterial inactivation [94–97].

Virions, the entire infectious virus particle, have the simplest compositions as they consist on a nucleic acid and an outer shell of protein (capsid), which may vary among viral genus [98]. MS2 coliphage it is one of the most resistant viruses (excluding adenovirus) to UV inactivation [99]. Very few works have been performed using viruses as target of inactivation by solar photo-Fenton, where photo-oxidation of the capsid seems to be the main way to inactivation [92,93,100].

Spores of *F. solani* are a robust survival form; cell wall is a rigid structure composed mainly of polymeric sugars (like glucans, mannans, and chitin), proteins and glycoproteins [101]. Furthermore, the influx of oxidative reagents like H₂O₂ or iron to the cells core is inhibited in spore forming phase, while influx of these species may occur during germination processes, favored by solar light and presence of organic matter (sugars, alcohols, organic acids, amino acids) [102]. Therefore, there are big differences on the behavior

of spores as compared to vegetative cells, being more resistant to disinfection process [79].

On the other hand, the external cell wall composition of spores of Sulphite-Reducing clostridia (SRC) is one of the most resistant biological structures; it is made of four layers covering the spore core. They are an outer proteinaceous coat, which provides chemical and enzymatic resistance, followed by a peptidoglycan thick layer, which high resistance to temperature up to 80 °C, and then followed by a typical Gram-positive structure of cell wall (layer of peptidoglycan and inner membrane), which acts as permeability barrier. Other species-specific structures and chemicals associated with endospores include stalks, toxin crystals, or an additional outer glycoprotein layer called the exosporium [103,104]. This highly protective structure confers special resistance to SRC spores against multiple disinfection techniques [105], as well as for photo-Fenton even at acidic pH [25,93].

Furthermore, novel water pathogens are of concern in reuse of treated secondary effluents (See Table 2). It is suspected that secondary effluents are the main anthropogenic source of antibiotic resistant bacteria (ARB) and antibiotic resistant genes (ARG) release into the environment. ARB and ARG can be spread into the environment, resulting in a decrease of antibiotic therapeutic potential of pharmaceutical products against animal and human pathogens and, finally, it may pose a severe risk to public health in water sources and environment [31]. Inactivation of naturally occurring ARB and ARG in secondary effluents is a challenge, since ARB has been demonstrated to be in general more resistant to disinfection techniques than common waterborne microorganisms [31]. Recently, research studies have been assayed to find out the capability of several solar driven photocatalytic processes to remove ARB from secondary effluents. A comparative study of inactivation efficiency of near neutral pH photo-Fenton, titanium dioxide and sunlight with added H₂O₂ (0.5–2.2 mM) at neutral pH demonstrated that solar photo-Fenton was not competitive in terms of efficacy in the removal of ARB as compared with using H₂O₂ and sunlight. Moreover, the antibiotic resistance genes of survived colonies were not affected by these processes [106–108], having

these ARB and ARG special resistance to solar AOPs under mild conditions (neutral pH and low amounts of Fe and H₂O₂).

3. Chapter II: effect of the operational parameters—shifting the equilibrium of the photo-Fenton process

3.1. Fenton reagents (Iron/H₂O₂)

The most common reagents used for conventional photo-Fenton are iron (mainly ferrous sulphate (Fe²⁺) or ferric nitrate (Fe³⁺)) and hydrogen peroxide. The efficiency of the process depends on a number of parameters already mentioned in previous sections, such as pH, temperature, but also the concentration of both reagents used; this should be taken into account to achieve high inactivation rates of the selected microorganisms. In general, the higher iron and hydrogen peroxide concentration, the higher oxidation rates [109]. Nevertheless, an excess of iron ions or H₂O₂ limits and/or inhibits the solar process efficiency, due to the species that may act as scavengers of hydroxyl radicals, according to the following equations:



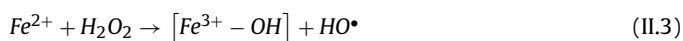
The typical range of iron concentration used for solar photo-Fenton for water decontamination, ranges from 0.01 to 1 mM, reporting an increased reaction rate with the increase on iron concentration [110–112]. In general, for disinfection, the iron concentrations (Fe²⁺ or Fe³⁺) lower than 0.2 mM are typically used. Due to the already discussed influence of pH in the iron solubility, most of the iron is precipitated at neutral or near neutral pH, being effective or photo-active only very low amounts of iron. Some authors have reported successful results for water disinfection using concentrations lower than 0.02 mM of iron independently of the iron added to the sample from 0.02 to 0.2 mM [12,79,80,113]; while concentrations higher than 1 mM (50 mg L⁻¹) at near neutral pH could not be desirable for water disinfection as the precipitated iron and aggregates and colored suspended solids generated affect negatively to the light penetration and therefore decreasing the microbial inactivation efficiency [11,12,17].

Iron is one of the most abundant elements on the Earth's surface, and therefore, it can be found in natural waters. Several studies on water disinfection using photo-Fenton have been carried out with natural waters containing very low concentrations of iron [15,21,22,114]. These authors have demonstrated the enhancement of the inactivation of total coliforms, *E. coli* and *Salmonella* in PET bottles and 25L-CPC reactors by photo-Fenton considering only the presence of natural iron present in the natural water. Through these studies performed in the Sahelian region, high bacterial inactivation rates have been reported, attributed to photo-Fenton process occurring in the presence of natural iron concentration ranged from 0.01–0.05 mg L⁻¹ (0.2–0.9 μM) in the raining season to 0.06–0.07 mg L⁻¹ (1.1–1.2 μM) and 0.10 mg L⁻¹ (2 μM) in the dry season, and the addition of low concentrations of hydrogen peroxide (10 mg L⁻¹, 0.3 mM). These results demonstrated that the iron content in natural water is enough to drive an efficient photo-Fenton process leading to total bacterial inactivation when adding H₂O₂ [15,21,22,114].

Other key parameter for photo-Fenton efficiency is the initial ratio of Fe to H₂O₂ which vary from 1 to 5–10 wt/wt of Fe²⁺ to H₂O₂ [115]. Common molar ratios of Fe²⁺:H₂O₂ of the Fenton's Reagent for water disinfection are in the range of 1:2, 1:9, 1:14; 1:18. Nevertheless, it has been demonstrated that ratio 1:2 is enough for achieve good inactivation results [116], even for disinfection of secondary effluents [20,80,93].

Some contributions have explored different strategies to carry out photo-Fenton for water and wastewater disinfection applications regarding the addition of iron and H₂O₂. They can be summarized as follows:

i) *Strategy of addition of reagents at the beginning of the process*: This strategy is one of the most commonly used for water disinfection. It consists on the addition of the reagents to the water sample at the beginning of the process without any further adding of reagents. This process is monitored in terms of microorganism concentration, hydrogen peroxide, and dissolved iron concentration present in the sample throughout the experimental time. As H₂O₂ is consumed during photo-Fenton, the photo-Fenton Reactions (II.3) and (II.4) are slowed down dramatically or limited during the process, giving rise to the other reactions where iron may react with the microorganisms, as well as internal photo-Fenton reactions. With this strategy, very good inactivation results have been reported for inactivation of different microorganisms such as *E. coli*, *E. faecalis*, *Fusarium solani*, etc. in different water matrixes (Distilled water, synthetic and real secondary effluents) [12,79,80].



ii) *Addition of iron at the beginning of the process and dosage of H₂O₂ during photo-Fenton process*: This strategy is the most used for water decontamination by solar photo-Fenton, as the dosage of H₂O₂ during the solar process ensures that Reactions (II.3) and (II.4) are not limited at any moment, thus provoking the maximum capability for the generation of HO[•] and the best decontamination rates for organic pollutants removal [117]. From the point of view of water disinfection this strategy also showed a better inactivation rate compared to the first one. Polo-López et al., investigated the effect of both strategies on the inactivation of spores of *F. solani* in different types of water. They observed a clear enhancement for both, the inactivation of fungi spores and degradation of organic matter in wastewater adding sub-sequent dosages of H₂O₂ compared to one single addition at the start of the process [80]. Nevertheless, in this case it should be remarked that a higher consumption of H₂O₂ was noted during the duration of the process, and therefore, a higher cost is possibly implicated.

iii) *Dosage of iron during solar photo-Fenton process*. Additionally, the effect of hydrogen peroxide and iron dosage was evaluated for the solar photo-Fenton treatment in compound parabolic collector photo-reactors at neutral pH for the inactivation of wild enteric *Escherichia coli* and Total Coliforms (TC) present in secondary effluents of a municipal wastewater treatment plant [24]. They demonstrated that photo-Fenton with iron additions (20, 10 and 10 mg L⁻¹ of Fe²⁺ every 5 min with 50 mg L⁻¹ of H₂O₂ as unique initial dose) slowed down the disinfection rate with regard to a unique iron addition (20 mg L⁻¹, with H₂O₂ at 50 mg L⁻¹) as inactivation time increased from 45 min to 90 min for *E. coli* and from 80 to 120 min for TC. Nonetheless, hydrogen peroxide consumption was higher using the iron dosage mode than with one iron addition, since more H₂O₂ reacted with iron every time fresh Fe²⁺ was added.

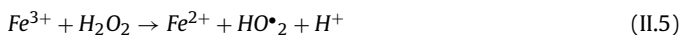
iv) *Increasing hydrogen peroxide concentrations*. For the case of secondary effluents, it is clear that the presence of organic matter in the water matrix will compete for oxidative radicals generated during photo-Fenton. For that reason, it is reasonable to believe that an increase in hydrogen peroxide will permit better disinfection rates and therefore to reduce treatment time to

achieve desirable disinfection results. This has been explored by Ortega Gómez et al. [11]. They compared two conditions at near neutral pH of photo-Fenton, 20 mg L⁻¹ Fe²⁺ and 50 and 100 mg L⁻¹ of H₂O₂. When the concentration of hydrogen peroxide increased from 50 to 100 mg L⁻¹, inactivation times by photo-Fenton were reduced by 33% and 25% for *E. coli* and TC, respectively, although the amount of residual hydrogen peroxide was increased twofold. Consequently, doubled initial hydrogen peroxide concentrations induced little enhancement in disinfection times and the addition of iron is not a practical strategy.

3.2. Temperature

Water temperature plays a different role during any water treatment, as this parameter will not only affect the chemical reaction but, more especially, the microorganisms' response to the treatment and thus to the disinfection rate. For this reason, temperature becomes a key parameter in disinfection processes, and therefore it may be used in favour of the treatment efficacy for reducing the cost in reagents and treatment time. In particular, temperature during photo-Fenton water disinfection will affect both iron and H₂O₂ reactions kinetics and microorganisms. It is well known that increasing temperature had a beneficial effect on reaction kinetics. For solar-promoted processes, the common water temperatures will typically range from 10 to 45 °C which is the most common environment temperatures recorded in areas with high solar irradiance and therefore susceptible of use photo-driven processes by sunlight such as photo-Fenton reactions [63].

- i) *Effect of temperature on iron.* Iron solubility may vary depending on temperature of water solution. Several works in literature have reported increasing degradation rates by photo-Fenton by raised temperature values from 20 to 50 °C, based on photo-Fenton reactions against both organic compounds (TOC) and microorganism. Gernjak et al. found a 5 times higher TOC degradation rate by raising temperature from 20 to 50 °C at 2.6 mM as maximal iron concentration [110]. Another contribution [118] reported maximum photo-Fenton process efficiency at around 55 °C. Nevertheless, they observed that temperature had an important effect in the organic matter degradation, especially when the ratio of Fenton reagents was not properly chosen. This effect has not been always observed and in some cases the effect of temperature in the catalytic process prevails. The reason is that the activity of thermal Fenton/photo-Fenton processes is remarkable for values around 50–75 °C [119], or even higher (e.g. 100 °C, but for pressurized systems) [120]. A decrease in photo-Fenton efficiency, attributed to iron precipitation with increased temperature (50 °C), has been reported for water decontamination at acidic pH values [121,122].
- ii) *Effect of temperature on hydrogen peroxide.* In general, for this compound, temperature increase enhances H₂O₂ decomposition [123]. On the other hand, H₂O₂ consumption in water can be favoured by thermal reactions involved in the reduction of ferric iron, particularly Eq. (II.5) [63] without producing OH•, while in the photo-reduction pathway of ferric iron H₂O₂ is not consumed. Therefore, the optimal temperature for photo-Fenton has been reported to be ca. 30 °C, as above this value, H₂O₂ tends to be thermally decomposed into H₂O and O₂ [124].



- iii) *Effect of temperature on microorganisms.* The disinfecting effect of high temperatures is well known as pasteurization. Thermal increasing beyond the optimal temperature of each

microorganism and strain, drastically reduce the viability of microorganisms due to loss of integrity of proteins, enzymes and genetic material. The optimal temperature for the most bacteria is between 35 and 40 °C; while it is around 28 °C for the most of the fungi [125]. It is therefore expected that any disinfection process would be strongly marked by temperature. As far as the generation of oxidative species in SODIS is concerned, it's also expected that temperature is a key parameter having important influence over the disinfection rate. Solar disinfection bactericidal effect is attributed to the synergistic effect of UV solar radiation and solar mild heating produced over periods of solar exposure typically of 5–6 h [89]. Water temperatures reached during solar disinfection of water range from 20 to 55 °C. A strong synergistic effect has been observed between optical and thermal inactivation processes for water temperatures exceeding 45 °C [126]. This was explained by McGuigan et al., by the addition to a slow pasteurizing effect, as elevated water temperatures inhibit the DNA repair mechanisms. In this sense, the effect of temperature over solar water disinfection process efficiency is deeply reported in the literature [127–129]. In synthetic secondary effluents this tendency has been also confirmed by Giannakis et al., who reported the sensitive light-temperature synergy in the inactivation of *E. coli* by SODIS, at irradiation values of 800 and 1200 W m⁻² with temperatures of 50 and 60 °C [130,131].

In this line, the positive effect of water temperature increase over disinfection rate for other oxidizing process like heterogeneous photocatalysis has been also investigated at temperatures between 15 and 45 °C under natural solar radiation [132]. Briefly, they attributed this effect briefly to three facts acting simultaneously: (i) an increase in generated •OH by TiO₂; (ii) an increased activity of the chemical reaction kinetics associated to the metabolic activity; and (iii) the non-lethal influence of temperature on the microorganisms studied.

Very few works have investigated the thermal effect of photo-Fenton for water disinfection. Recently Ortega-Gómez et al. showed an enhanced *E. faecalis* inactivation as temperature increased from 10 to 40 °C. They also reported an initial reduction of the dissolved iron concentration at neutral pH, and the higher iron precipitation with increasing temperatures. Nevertheless, after 60 min of reaction, 40% of the initial iron concentration remained in solution (available for photo-Fenton reactions), obtaining an enhancement of the treatment efficiency of 50%, with an increase of 20 °C in the temperature [18]. These authors attributed this thermal enhancement to the influence of temperature over microorganisms. *E. coli* and *E. faecalis* can be cultivated in the range of 10–47 °C, with optimum temperature at 37–44 °C [125]. When temperature is far from the optimal values, significant changes in the metabolism of cells occur. At temperatures below 10 °C, the fluidity of cell membrane is drastically reduced and its metabolism slows down. At the optimum temperature, the metabolic activity is maximal; the genetic material is unpacked and completely active; therefore the microorganism is more vulnerable to oxidative stress due to increased surface of DNA [18]. Beside, the repair of DNA damage induced by the so-called SOS response is reduced in *E. coli* when temperature increases from 10 to 20 °C, being constant until 40 °C has been proven [133]. Therefore, photo-Fenton reaction taking place at mild-temperatures, near the optimum growth temperature for bacteria, may produce more damages by oxidative attack of OH•, suggesting that the mechanism of death may be more related to processes taking place inside the cells rather than from the external concentration of radicals [18].

3.3. Solar radiation: irradiance, cumulative dose & time

The photo-Fenton process has been investigated at pilot and demo scale in solar plants, thanks to the availability of this process to be driven by natural solar photons. The role of solar photons on the photo-Fenton reactions is the photo-reduction of hydrated ferric ions ($[\text{Fe}(\text{OH})]^{2+}$) to ferrous ions giving rise to hydroxyl radicals; being responsible for this reactions photons with wavelengths shorter than 580 nm [84,134].

Several radiation parameters can be considered to evaluate the microbial inactivation using solar photo-Fenton such as: (i) the total amount of solar UVA energy received per unit volume of treated water, Q_{UVA} , kJ L^{-1} ; (ii) the cumulative solar UV dose (J m^{-2}) or (iii) the experimental time [63]. In solar-promoted processes, it has been demonstrated that the efficiency of the bacterial inactivation increases at higher solar energy doses when the process is either produced by the mere action of solar photons like solar water disinfection in photo-reactors [135], or by other photocatalytic processes, including heterogeneous photocatalysis [136] and photo-Fenton [16]. Nevertheless, the relationship between microorganism photo-inactivation rate and solar exposure time, energy received, or dose applied is not completely elucidated today.

3.3.1. Volumetric cumulative solar UVA (Q_{UVA})

This parameter is the most used to assess solar photocatalytic processes for water decontamination under natural sunlight; it has been also used to assess the microorganism's inactivation from water [63]:

$$Q_{\text{UV}} = \int_{t_1}^{t_2} I_{\text{UV}}(t) \frac{A_r}{V_T} dt \quad (\text{II.6})$$

where t_n is the experimental time for n-sample, I_{UV} is the incoming solar irradiance in the UVA range measured (W m^{-2}) at any time (t , s), A_r is the illuminated surface (m^2), and V_T the total water volume (L).

3.3.2. Cumulative solar UVA dose

This parameter defines the solar UVA irradiance received in the sample in a given time (Eq. (II.7)):

$$\text{Dose}_{\text{UV}} = \int_{t_1}^{t_2} I_{\text{UV}}(t) dt \quad (\text{II.7})$$

where I_{UV} is the incoming solar UVA irradiance in terms of W m^{-2} , at time t (s).

3.3.3. Treatment time

The experimental time is not often used when irradiation is provided by natural sunlight, as solar irradiance values vary constantly; nevertheless under constant illumination like in a solar simulator, time is a good option as parameter to deal with the inactivation rate of microorganism and the efficiency of the process.

In the case of photo-Fenton, there are very few contributions investigating the role of the accumulated energy dose (in terms of total energy received in the system per unit of volume, kJ L^{-1}) and irradiance (solar intensity, in terms of W m^{-2}) in the inactivation of pathogens during the solar photo-Fenton process at neutral pH [15,16]. It also should be noted that solar irradiance has itself a deleterious effect on the viability of microorganisms in water [89]. Therefore, during solar photo-Fenton treatment application for water disinfection there are many reactions and processes involved in the inactivation rate working simultaneously; those which are mainly for the generation of HO^\bullet , and others dominated by UVA absorption followed by ROS generation (solar photo-inactivation).

Ndounla et al. did a comparative evaluation of photo-Fenton disinfection rates as a function of different irradiation periods,

based on the monitoring of the effective disinfection time (EDT), or required time to acquire the total inactivation of targeted bacteria in defined conditions of a solar CPC photo-reactor. They observed a significant impact of the irradiance on the process; high average irradiance of 35 W m^{-2} led to the total inactivation of *Salmonella* spp. in an EDT of 45 min and a dose of 26 Wh m^{-2} ; while low irradiance of 20 W m^{-2} required an EDT of 180 min for a dose 60 Wh m^{-2} . Thus, these results revealed that lower irradiance level led to higher doses to achieve the bacterial disinfection [15]. Similarly, the recent contribution of Ortega-Gómez et al., reported an improved inactivation rate of *E. faecalis* by solar photo-Fenton at neutral pH with increased irradiance in the range of UVA irradiances between 10 and 30 W m^{-2} in a batch reactor with non-concentrated solar light. Results demonstrated that the inactivation rate was limited by solar UVA irradiance, as the first order rate constants followed a linear correlation with irradiation, indicating that bacterial inactivation was photo-limited in the $10\text{--}30 \text{ W m}^{-2}$ UVA range. This photo-limitation phenomenon was also observed for the H_2O_2 consumption rate: a linear relationship was observed between $k_{\text{H}_2\text{O}_2}$ and irradiance. Therefore, an increase in the radiation intensity resulted in a higher oxidizing agent consumption rate and consequently, in higher HO^\bullet production, giving an increase in the rate of bacterial inactivation. Regarding the accumulated energy per unit volume (kJ L^{-1}), which combines irradiance and solar exposure time, bacterial inactivation follows a first order kinetics with Q_{UVA} regardless of the irradiance. To achieve a given bacterial inactivation degree, the lower the irradiance, the longer the required exposure time. Therefore, in the case of photo-limited conditions, Q_{UVA} is an adequate parameter for the kinetic characterization required to make predictive models for reactor design and up-scaling for large wastewater disinfection systems with solar photo-Fenton [16].

3.4. Photo-reactor parameters

The design of photo-reactors for water disinfection using solar photo-Fenton requires the evaluation of different parameters, apart from the already discussed ones, as reagent concentrations, temperature, solar radiation intensity, dose, etc. Herein, other important parameters for the proper design of photo-reactors for water disinfection are discussed.

3.4.1. Residence time in the photo-reactor

This parameter is of high importance for up-scaling photo-reactors, which require the flow system to permit the treatment of large volume of contaminated water and also for microorganisms; it has been especially described for SODIS (solar disinfection) applications that microorganisms may recover during their presence in dark areas of the reactor, or even after the solar exposure process. As mention before, the residence time for inactivation of bacteria was found early in 2004 as a fundamental parameter for design of solar reactors, destined for disinfection of water. Rincón and Pulgarín, defined the above mention effective disinfection time (EDT) as the required time to acquire total inactivation of targeted bacteria in specific conditions, which also guarantee the absence of bacterial regrowth afterwards [4]. Later, it was demonstrated that in order to achieve complete bacterial inactivation, an uninterrupted, continuous UVA dose was much more effective than the same UVA dose delivered in an intermittent manner, regardless the source of sunlight, either artificial or natural [4,135]. This was also proven with solar CPC reactors under natural solar radiation [135,137]. Therefore, residence time of bacteria plays a key role both in solar photo-inactivation and solar photocatalysis for scaling-up of continuous flow reactors. On the other hand, it is important to note that the use of solar photo-Fenton in recirculating flow reactors has the advantage of non-stop the reactions, such as Fenton reac-

tions, which can occur in the dark areas of the reactor, therefore excluding microbial repair processes during the treatment.

3.4.2. Water turbidity

As in any process driven by photons (solar and lamps) the presence of suspended solids and turbidity reduce the efficiency of the process. The presence of suspended particles in the water will vary from acting as scatter of the light to the complete limiting of the solar treatment, by hindering the penetration of the light in the water; this will depend on the amount of particles and the turbidity of the treated water. Therefore, water turbidity is not desirable for solar treatments, even at low concentration because suspended particles such as faecal material, solid materials, etc., protect the microorganisms against radiation. Contaminated turbid water may be pre-treated using simple and low cost filtration system to remove as much as possible of the suspended particles in the water before treatment with solar process. Therefore, it is important before intending to address water disinfection by photo-Fenton to evaluate its efficiency on disinfecting large volumes of natural clear water of turbidity less than 30 NTU, as recommended in SODIS references [22,138].

3.4.3. Spectral transmission of photoreactor materials

The choice of materials that are resistant to solar aging and transparent to sunlight, mainly in the UV range, is limited. Fluorinated and acrylic polymers and several types of glass meet these criteria. For example, fluoropolymers are a good choice due to their high UV-transmittance and chemical stability. However, the wall thickness of the photoreactor has to be increased to gain the required minimum operative pressure resistance and therefore decreasing the UV transmittance [139]. Quartz has the best available UV transmittance, as well as good thermal and chemical resistance, but its high cost makes it completely unfeasible for large-scale solar photocatalytic applications. Standard glass adsorbs a part of the near-UV solar radiation, due to its high iron content [140]. Low-iron borosilicate glass has good transmittance in the solar range to about 285 nm (Pyrex or Duran). Moreover, when this type of glass is exposed to UV-solar radiation, it is photo-aged with subsequent reduced UV transmittance, which is attributed to the valence changes in metal ions in the glass; Fe^{2+} undergoes transformation to Fe^{3+} , therefore absorbing UV light. This problem may be solved using low iron content glasses to less than 100 mg kg^{-1} [141].

With the aim of reducing costs, other materials could be also used for solar disinfection in developing countries, with the corresponding losses in UV transmissivity. That was the case of commercial methacrylate, which was shown as a feasible option for low-cost solar disinfection photo-reactors [142]. This material has a cutoff wavelength in the UVA range, with obvious direct consequences on the germicidal action of solar radiation and also less solar UVA transmission as compared to borosilicate glass (Duran), quartz and PET (polyethylene terephthalate) bottles, which have a relatively high transmission due to their very low wall thickness. However, it has the advantage of robustness and a lower cost than any system constructed from other commercially available materials (see Fig. 2).

4. Chapter III: unconventional photo-Fenton reaction

When implementing the photo-Fenton reaction in water treatment for real applications, a pre- and pos-treatment process would be required to achieve the best efficiency by photo-Fenton at the working pH, which would potentially increase the cost of the treatment. This situation is due to the most desirable working pH for the reaction occurs at pH 2.8–3.0. Beyond these values, the amount of iron ions decreases drastically, forming Fe^{3+} precipitates after its

transformation from Fe^{2+} , due to its extremely low solubility product constant, even at pH 4.0. Therefore, this situation calls for new research on strategies to operate this process at relatively small iron concentrations and near neutral pH, with a high efficiency for disinfection and reduced costs. Some research is based on modification of physico-chemical characteristics of the water and use of complexing agents to increase iron solubility at near neutral pH.

4.1. Iron oxides/NanoSize iron oxides

Iron oxides are one of the most important transition metal oxides of technological importance. To date, sixteen pure phases of oxides, hydroxides and oxy-hydroxides are known. Iron oxides are composed of Fe(II) and/or Fe(III) cations and O_2^- and/or OH^- anions [143]. The main advantages of nano-iron are their relatively low toxicity and biodegradability, abundance in nature and ease to synthesize in the laboratory. Examples of iron oxides for water treatment research are: hematite ($\alpha\text{-Fe}_2\text{O}_3$), magnetite (Fe_3O_4), maghemite, $\beta\text{-Fe}_2\text{O}_3$, $\varepsilon\text{-Fe}_2\text{O}_3$, goethite, ferrihydrite, lepidocrocite and wüstite (FeO).

Most of these solid iron oxides have shown semiconductor properties and therefore, they may also act as photocatalysts [144]. The efficiency of these iron (hydr)oxides for inactivation of microorganisms in water at near neutral pH has been reported, demonstrating the capability of iron oxides acting as semiconductor via a photocatalytic process and as an heterogeneous iron source in Fenton process at near neutral pH [14,145–148].

Some adsorption processes for wastewater treatment have utilized ferrites and a variety of iron containing minerals, such as akaganeite, feroxyhyte, ferrihydrite, goethite, hematite, lepidocrocite, maghemite and magnetite [149]. Although not any real application of iron oxides for disinfection of MWWTPs secondary effluents has been done to date, the effect of DOM and inorganic substances on the efficiency of iron (hydr)oxides for bacterial inactivation has been reported recently. Ruales-Lonfat et al., demonstrated that NOM and inorganic substances did not interfere with the photocatalytic semiconducting action of hematite to bacterial inactivation. However, these components enhance the bacterial inactivation by heterogeneous photo-Fenton action of hematite due to the possible complexation and solubilization of iron by NOM, which, in turn, may favor the process [13].

4.2. Supported iron/nano-materials

Different kinds of support have been used to immobilize iron such as metal oxides, zeolites, carbon nanotubes, fibers, etc. revealing promising results for further application as water disinfection technology. The desired properties of a support for Fe-ions immobilization are: (i) high chemical resistance against the highly oxidative radicals formed during reactions in solution, (ii) stability of the immobilized iron and reduced leaching of Fe ions from the support, (iii) high capability for target removal, and (iv) long-term stability of the support during operation [150]. Among the most sustainable support materials for iron ions in reactor processes are the woven fibrous glass fabrics, as they present an open microstructure, with adequate mechanical and thermal resistance [151,152]. Silica fabrics have been recently reported useful in oxalic acid degradation, showing adequate stability and low Fe-ions leaching [153]. As an example, Moncayo-Lasso et al., tested a woven inorganic silica fabric loaded with Fe-ions (EGF-Fe) for the inactivation of *E. coli* in water. These authors demonstrated that photo-Fenton process with EGF-Fe fabric is a suitable solar heterogeneous catalyst to remove hydroquinone and *E. coli* at a near neutral pH in the presence of low concentration of H_2O_2 and with a low amount of iron leached in solution [9].

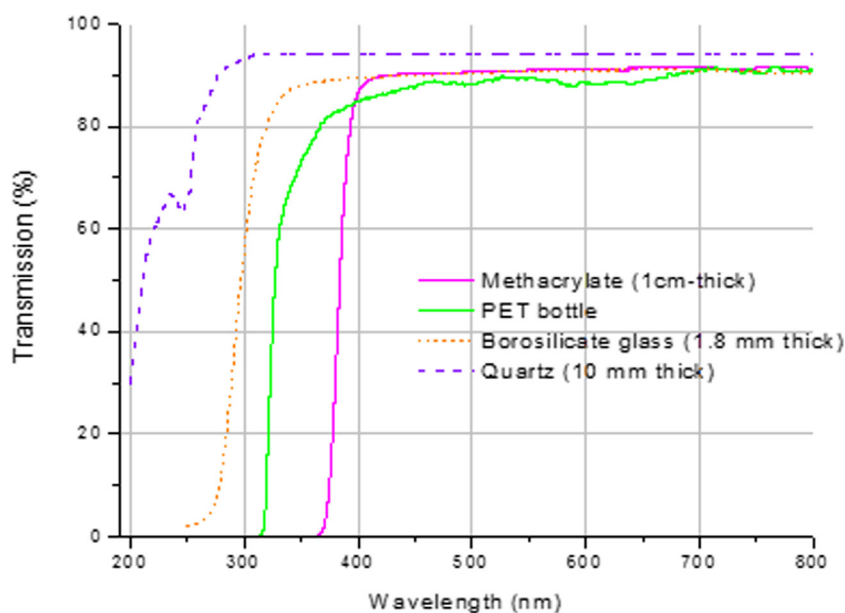


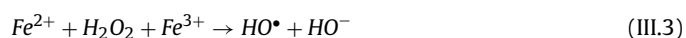
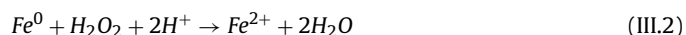
Fig. 2. Transmission spectrum of several materials commonly used as photo-reactors for solar water treatment.

Iron oxide (Fe_2O_3) nanoparticles supported onto glass fibers for microbial inactivation in water has been also investigated, such as silver-coated hematite, ($\alpha\text{-Fe}_2\text{O}_3$), nanoparticles and hematite alone displaying antiviral properties against the model virus, MS2 phage [154,155] and bacteria, specifically *E. coli* [155]. Other silver-doped iron oxides, such as CuO/Ag and $\text{Fe}_x\text{O}_y/\text{Ag}$ immobilized on fiberglass, have been investigated due to well-known antibacterial properties of this metal. Immobilization of silver nanoparticles inlaid $\text{Fe}_3\text{O}_4\text{-SiO}_2$ magnetic composite ($\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-Ag}$) also has shown great potential as an antibacterial material in water for disinfection [156].

The use of membranes as polymer supports for iron oxides has been widely investigated for removal of chemical compounds in water; however their potential application for water disinfection has not yet been well developed.

4.3. Zero valent Iron(ZVI)/nanoscale zero valent iron (NZVI)

Over the last decades, research has been also focused on zero-valent iron (ZVI) to treat contaminated groundwater and wastewater using this reactive metal as it is abundant, non-toxic, low cost, and easy to produce. ZVI has a standard redox potential of $E^0 = -0.44\text{ V}$, being an effectively reductant when combining with oxidized contaminants by transferring electrons. Moreover, degradation of organic matter in the presence of dissolved oxygen and ZVI occurs according to the following reactions:



Most research has been focused on the degradation of chemical pollutants such as trichloroethylene, nitrate, arsenic, Cr(IV) , phenol and nitrobenzene [157]. Nevertheless, ZVI also has shown promising results on the removal of relevant contaminants in drinking water, including viruses and bacteria, chlorine, disinfection by-products (DBPs), DBP precursors (e.g., natural organic matter), and metal ions [143].

ZVI results suggested that this treatment may be useful for drinking water treatment and can potentially give a number of benefits, thanks to the capability of ZVI to remove NOM, arsenic

and microorganisms, preventing further DBPs formation like those generated by, for example, chlorination. The first report about ZVI capability for water disinfection was confirmed through the inactivation of waterborne viruses MS2 and ϕX174 (5-log reduction in 20 min) [158]. Since then, other contributions have shown promising results using ZVINP for inactivation of bacteria, viruses and fungi [159–161]. Aspects related with the presence of oxygen have been also investigated, demonstrating that *E. coli* inactivation rate decreased with time under aerobic conditions, whereas it increased under anaerobic conditions. Lee et al., reported that cells treated under anaerobic conditions exhibited dark spots in their internal wall and cytoplasm; those spots were formed due to oxidation of Fe(II) to Fe(III) inside the cell damaging the cellular components and respiratory activity by oxidation under anaerobic conditions. The inactivation rate of MS2 can as well be enhanced by increased ZVINP concentrations under aerobic or anaerobic conditions [159,160]. The effect of acidic pH was also investigated for the inactivation of MS2. Virus inactivation was increased with decreasing pH as higher activity of HO^\bullet was observed at lower pH [160].

The inactivation mechanisms identified by these authors are based primarily on the irreversible adsorption and inactivation of microorganism by direct contact to the nanoparticle (NP). The interaction between ZVINP and bacteria lead to disruption of cell wall by the effects on the protein functional groups and lipopolysaccharides, driven by reductive decomposition [159]. It is also suspected that surface corrosion of ZVI might create more oxide particles for direct contact and new sites for adsorption [158]. Furthermore, ZVINP oxidation in aerobic conditions ended in the formation of two oxy-hydroxides phases: lepidocrocite ($\gamma\text{-FeOOH}$) (at high $\text{O}_2/\text{Fe(II)}$ ratio and fast Fe(II) oxidation rate under abiotic conditions) and magnetite (Fe_3O_4) (at low $\text{O}_2/\text{Fe(II)}$ ratio and slow Fe(II) oxidation rate under biotic conditions) under neutral pH and ambient temperature; iron(II) species was more toxic to bacteria than Fe(III) . Auffan et al., assessed the ZVINP effectiveness on *E. coli* Qc1301 and mutant *sodA sodB* Qc2472. They observed a high concentration of lamellae-shaped ZVINPs in the cell membrane and three possible mechanisms for bacteria inactivation by ZVINPs were proposed: (i) disruption of membrane integrity; (ii) limitation of electron and ion influx and efflux system in cells; and (iii) ROS generation and SOD (superoxide dismutase) reduction [162].

In the case of viral inactivation, the formation of reactive species in the presence of oxygen or direct contact is also described as the main causes of death. ZVINP generally attacked the capsid protein inducing potential damage to the RNA [160,163].

A latter study using different kinds of microorganisms (*B. subtilis* like Grampositive bacteria, *P. fluorescens* like Gram-negative bacteria and *Aspergillus versicolor* like a fungus) demonstrated that efficiency of ZVINP depends not only on the state of ZVI (oxidized or not), but also on the composition of cell walls. The inactivation rate found in increasing order was: *P. fluorescens* (inactivated by both oxidized and non-oxidized ZVINP) < *B. subtilis* (inactivated by oxidized ZVINP about 80% of while about 99% by non-oxidized ZVINP) < fungi (survival rate above 90% in both ZVINP conditions). It was described that the extremely rigid fungal cell wall has avoided the internalization of ZVINPs, thus limiting their fungicidal capacity. The reaction of ZVINP and lipoteichoic acid in gram-negative bacteria created chelating complexes to hinder the natural cell operation system, due to the lipoteichoic acid shortage which is responsible for maintaining cell shape, autolytic enzyme activity and homeostasis management [161].

Unlike the clear advantages showed by ZVINPs for drinking water treatment, there are still some challenges in the practical application of ZVINPs such as: (i) the need of anaerobic condition; aerobic environments can decrease the corresponding antimicrobial activity [161]; (ii) some corrosive products such as FeOOH, Fe(OH)₂, Fe(OH)₃, Fe₂O₃, Fe₃O₄, or green rust can be formed onto metallic surface and obstruct pipe lines in water distribution system; (iii) the aggregation of ZVINPs can reduce the efficiency of the disinfection process; (iv) immobilizing a ZVINP system would decrease the exposed surface, therefore reducing the efficiency during the disinfection process; (v) potential applications for groundwater remediation should take into account the unknown fate and transport of the ZVINP in aquifers [164].

4.4. Iron chelates

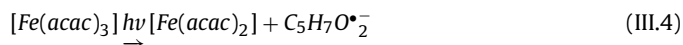
A different approach to reduce the problems encountered with the lack of efficiency of secondary effluents by photo-Fenton process at neutral pH lead to research focused on the use of compounds which are able to form complexes with iron in water, making it soluble for longer periods. Many iron chelates have been investigated for this purpose, such as polycarboxylate complexes like Ethylenediaminetetraacetic acid (EDTA) [165], citric acid and oxalic acid [165], nitrilotriacetic acid [166], tartaric acid [167] and humic acids [168]. There are several examples of ferrioxalate-assisted photo-Fenton for the degradation of contaminants in water at acidic and natural pH [169,170]. However, as most of these are not normally found in water and have to be added, toxicity and biodegradability of these substances also present important issues. The disadvantage of EDTA is that it is as a persistent organic pollutant generally forbidden and avoided due its capacity to solubilize heavy metals in water, which confers high toxicity levels [171].

Recently, the structural isomer of EDTA, (S,S)-Ethylenediamine-N,N'-disuccinic acid (EDDS) has been proposed as an attractive alternative to the former complexing EDTA mainly due to: (i) its biodegradability and therefore lack of toxicity [172,173]; (ii) its useful chelating capability for EDDS with iron(III) between pH 3 and pH 9, where the dominant form between pH 5 and 8 is FeL⁻ [174]. This photoactive specie has shown a high capacity for hydroxyl radical generation at neutral pH that permits to act independently of carbonate scavengers often present in natural waters [175]. EDDS has been also investigated for the treatment of secondary effluents with solar photo-Fenton at near neutral pH. Very promising results have been reported regarding removal of emerging contaminants in the concentration range of ng L⁻¹ to a few mg L⁻¹ (as found in municipal wastewater secondary effluents) [23,176–179].

On the other hand, limitations and disadvantages of Fe(III)-EDDS complex compared to conventional photo-Fenton have been also reported. (i) Low efficiency of Fe(III)-EDDS photo-Fenton at neutral pH due to less oxidative species than hydroxyl radical are formed (O₂^{•-}/HO₂[•]). (ii) High amounts of EDDS or even addition during the treatment are required to remove high concentrations of contaminants or to achieve mineralization, leading to a non-sustainable process with increased total organic carbon TOC. (iii) Unlike conventional photo-Fenton, it has been observed an efficiency reduction by temperature, which could present a problem when considering solar applications [175].

Unfortunately, application of EDDS for Fe(III)-EDDS photo-Fenton at neutral pH for wastewater disinfection has not been deeply investigated to date. Klamert et al., reported a first approach on the use of this chelate for secondary effluents disinfection [23]. This work showed a slight decrease of microbial load, observing the best results >3-log reduction of total coliforms in 120 min using a molar ratio of Fe:EDDS of 1:2 (0.1 mM of iron and 0.2 mM of EDDS) with 50 mg L⁻¹ of H₂O₂ at neutral pH. However, many aspects related to microbial inactivation by this process are unknown and it is expected new researches to increase the knowledge in this issue.

On the other hand, a strategy of using iron organic salts may be the solution to maintain iron in water at pH values far from acidic conditions. Recently, ferric acetylacetonate Fe(acac)₃ was used to promote solar photo-Fenton reaction for disinfection purpose [180]. They reported enhanced inactivation efficiency for the removal of *F. solani* spores in water at pH 5 (5–10 and 10–20 mg/L of Fe and H₂O₂) as compared to other inorganic iron salts like ferrous sulphate and ferric chloride. The nature of Fe(acac)₃, initially proposed by Bossmann et al. suggested that organic molecules serves as ligand in iron(III) complexes with a suitable oxidation potential, which is capable of undergoing highly efficient electron transfer to electronically excited Fe³⁺ to generate Fe²⁺ [134]. Since acetylacetonate possesses these characteristics, it may serve as ligand for the Fe³⁺ complex and also suitable for oxidation, acting in similar way as proposed for ferrioxalate reaction mechanism, as follows [181]:



Moreover, ferrous oxalate has been use as a source of hydroxyl radical starting from Fenton's reaction under certain conditions, compared to other organic ligands such as citrates [182]. Additionally, other authors reported successful disinfection results with photo-ferrioxalate for microorganisms like *Cryptosporidium parvum* [183] or *Escherichia coli* [5] at pH near to neutrality.

5. Chapter IV: applicability of near-neutral photo-Fenton & technological implications

5.1. Research and main experimental findings for pilot plant or full-scale applications

Up to now it is well established that one of the best solutions for pollutant removal and microbial inactivation by solar AOPs is the tubular photoreactor equipped with a Compound Parabolic Collector, the so-called CPC. CPCs are stationary collectors with a parabolic reflective surface around a cylindrical reactor. The main advantage of this system is the successful exploitation of the solar photons, as the reflector geometry reflects indirect light onto the receiver tube, and can therefore, capture both direct and diffuse sunlight. Other operational characteristics of these reactors are: static systems; use of non-imaging concentration optics with diffuse focus; homogeneous distribution of radiation into the absorber; constant concentration factor (CF: 1) for all values of sun zenith angle within the acceptance angle limit [63]. Fig. 3 shows a typical CPC pilot photo-reactor used for water disinfection.

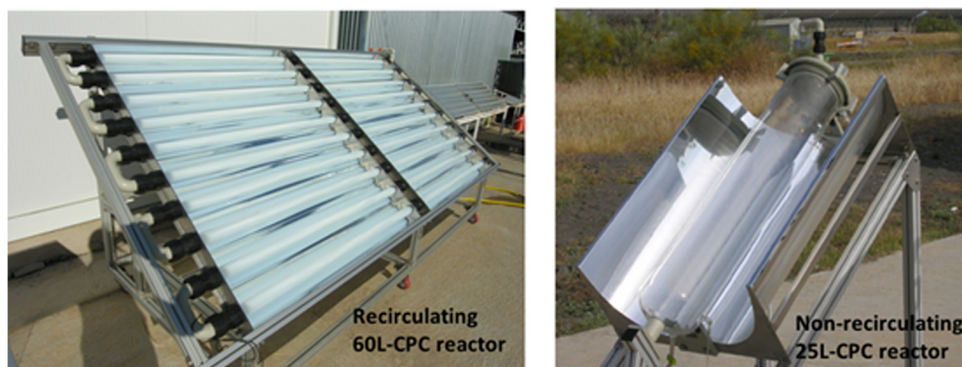


Fig. 3. Solar CPC pilot plans located at Plataforma Solar de Almería (Almería, Spain).

Table 3

Summary of articles on water disinfection by photo-Fenton at near-neutral pH carried out at solar pilot plant solar CPC reactors.

Source	Water volume (CPC reactor)	Water matrix	Microbial target	Best operational conditions	
				[Fe] (mg L ⁻¹)	[H ₂ O ₂] (mg L ⁻¹)
[73]	20 L	River water	<i>E. coli</i>	0.6	10
[23]	80 L	Secondary effluents	Total coliforms	Fe ₂ (SO ₄) ³⁺ : 5.58 +EDDS: 71.5	50
[184]	250 L	Secondary effluents	Antibiotic resistant (ofloxacin & Trimethoprim) Enterococci	Fe ²⁺ : 5	75
[93]	10 L	Secondary effluents	<i>E. coli</i> , Spores of Sulphite Reducing Clostridia, Somatic coliphages, F-specific RNA bacteriophages	Fe ²⁺ :10	20
[17]	7 L	Synthetic Secondary effluents	<i>E. faecalis</i>	Fe ²⁺ :20	50
[22]	25 L	Well water	Total coliforms, <i>E. coli</i> , <i>Salmonella</i> spp	Natural Fe: 0.01 Fe oxides: 0.23	10
[20]	20 L	Real & Synthetic Secondary effluents	<i>E. coli E. faecalis</i>	Fe ²⁺ :10	50
[25]	60 L	Secondary effluents	<i>Clostridium</i> sp	Fe ²⁺ :10	140
[15]	25 L	Well water	Total coliforms, <i>E. coli</i> , <i>Salmonella</i> spp	Natural Fe: 0.01	10
[24]	7 L	Secondary effluents	Wild enteric <i>E. coli</i> and total coliform	Fe ²⁺ : 20	50
[108]	60 L	Secondary effluents	Antibiotic resistant (clarithromycin & sulfamethoxazole) Enterococci	Fe ³⁺ : 5.02 pH 4	160
[80]	60	Real and Synthetic Secondary effluents	<i>Fusarium</i> sp No inactivation at natural pH	Fe ²⁺ : 5	60
[107]	8.5 L	Real Secondary effluents	Multidrug resistant <i>E. coli</i> to ampicillin, ciprofloxacin & tetracycline	Fe ²⁺ : 5.02	10
[114]	25 L	Natural alkaline surface water	Wild total coliforms, <i>E. coli</i> <i>Salmonella</i> spp.	Total Fe: 0.10	10

CPC reactor mirrors are usually manufactured from anodized aluminium, because they have high reflectivity in the UV-A range (87%–90%) and 90% for the visible and infra-red portions of the solar spectrum and are highly resistant to the environmental conditions. Most piping for connecting photo-reactors tubes and tank may be made of polyethylene or polypropylene due to the robust nature of these materials [140]. In recirculating reactors, water flows through the tubes to a tank using a centrifugal pump according to the reactor dimensions, and permitting a turbulent regime inside the photo-reactor tubes that favor the perfect homogenization of the water.

The use of solar CPC reactors for wastewater, secondary effluents and natural waters disinfection by photo-Fenton has been investigated recently (Table 3). The first application of photo-Fenton at CPC reactors for water disinfection was performed by Moncayo-Lasso et al., using river water and they demonstrated that the addition of low concentrations of Fe³⁺ (0.6 mg L⁻¹) in the presence of 10 mg L⁻¹ of H₂O₂ at near-neutral pH, leads to simultaneous decrease of TOC (55%) and total *E. coli* inactivation [73]. Since 2012, the use of solar photo-Fenton for secondary effluents disinfection

has been performed by several authors. In general, it has been demonstrated that low concentrations of added iron led to good bacterial and fungal inactivation rates of several kinds of microorganisms naturally occurring in secondary effluents at near neutral pH, leading also the simultaneous removal of present organic matter; a comprehensive list of works is given in Table 3.

5.2. Case studies for real applications

A variety of toxic compounds has been removed from water by solar photo-Fenton at demonstration and pilot-scale CPCs with collector areas ranging from 3 m² to 150 m² for micropollutants removal [63,139,184]. Unfortunately, there are no demo solar photo-Fenton plants for disinfection of wastewater to be used as tertiary treatment at large scale using CPC reactors up to now. Obviously, investment costs reduction is one of the most interesting ways to achieve the industrial applications of this solar treatment. These strategies have been addressed before for photocatalytic (heterogeneous) processes. An interesting option is the

use of an extensive and non-concentrating reactor such as Thin Film Fixed Bed Reactor (TFFBR), a Double Skin Sheet Reactor (DSSR) [185], application of shallow pond configurations and flat-plate reactors which were already studied in the nineties [186–188]. These options were avoided due to the low efficiencies found for the rates of pollutants compared to those found with CPC reactors under similar operational conditions. Nevertheless, from the point of view of costs, these alternative systems to CPC reactors could be an attractive option. This is due to the less hydroxyl radicals necessary and, consequently, less irradiance (less photons) to achieve efficient removal [189].

Recently, a Raceway Pond Reactor (RPR) has been used for micropollutant removal from secondary effluents using solar photo-Fenton (>99% TBZ and 91% ACTM reduction in 240 min with 25 mg L⁻¹ of Fe and 100 mg L⁻¹ of H₂O₂) [190]. This low cost solar reactor consists of an open reactor with channels through which the water is recirculated, with varied liquid depth and the flow is controlled. Materials used for built it are mainly plastic liners, therefore giving a low construction cost of about 100,000 Euro ha⁻¹, that is 10 Euro m⁻² [191]. Unfortunately, there is no information about the application of solar photo-Fenton for water disinfection using RPR. Nevertheless, we consider that further research will be done in the near future regarding this issue.

6. Conclusions

In this review the application of near neutral pH photo-Fenton as oxidative treatment for drinking water and wastewater effluents is attempted in a critical way.

All components involved in the global process, i.e., chemical, biological and physical parameters are differentiated and discussed individually, highlighting that the efficiency of photo-Fenton reaction depends on a number of factors playing an important role.

In brief, chemical composition of real wastewater plays a very important role being the main competitor for hydroxyl radicals and reducing the efficiency of the process. Remarkably, some organic matter, mainly humic substances (including aromatic and aliphatic structures, carboxylic, phenolic-OH, amino, and quinone groups) may enhance the disinfection efficacy of neutral-pH photo-Fenton, due to their role as either complexing agent that maintain iron in solution, or as photosensitizers that generate triplet stage forming other radical species that improve the rate of the process.

Biological nature of the target is surely also a key factor for this process. Susceptibility of a range of waterborne pathogens to photo-Fenton at near neutral pH has been investigated. Literature reveals a gradient of sensitivity like: non-forming spore bacteria < fungi < viruses < forming spore bacteria < helminths < protozoa. As well as, natural occurring pathogens clearly show a high grade of resistance to oxidative process as compared to lab-made strains. Eventually, complex mixtures of pathogens in different wastewater shall require additional investigation in terms of treatment and environmental resistance.

Solar photo-fenton efficiency for bacterial inactivation increases at higher solar energy doses, as for solar water disinfection and heterogeneous photocatalysis. Nevertheless, the relationship between microorganism photo-inactivation rate and solar exposure time, energy received, or dose applied is not completely clear today, as many parameters related to biological complexity and solar radiation variability, influence this process.

Therefore, as for solar reactors aspects, the main concept to consider is the optical characteristics of the water or wastewater in terms of light penetration and UV absorption by both, biological and chemical components including Fe-derived compounds. Optimisation of a solar photo-Fenton reactor needs maximization of treated water volume by proper choice of tube diameter. This

might be estimated as a function of light penetration properties of the solution; which ranges from decens of centimeters for very transparent water (<10 NTU) to few centimeters for turbid water (>30 NTU).

Finally, main research on up-scaling this solar process has been presented. Results derived from a number of studies in this matter show the capability of this solar AOP to be used at pilot scale; although more research is needed before application of this treatment at industrial scale, especially in terms of cost and treatment time reduction, maintaining its chemical and environmental sustainability with while bringing a good alternative for future wastewater reuse.

Unconventional approaches to the traditional photo-Fenton conducted at near neutral pH are also taken into account as these lines of investigation try to overpass the main limitations for wastewater effluents disinfection. Future research in this line has revealed very promising results for water and wastewater disinfection using iron oxides at near neutral pH, Zero Valent Iron and iron chelates such as EDDS. Nevertheless, more research in these lines is needed for optimization of process at pilot scale.

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